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For: RECORDING SHEET FOR INK JET PRINTING

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STATEMENT BY DR. JAKOB KUHN

Sir:

I, Dr. Jakob Kuhn, am responsible for patent related matters for ILFORD Imaging Switzerland GmbH, the assignee of the above-identified application. The application was filed in the English language in the United States Patent & Trademark Office ("PTO") on June 18, 1999 and claims priority to European Patent Application 98810556.5 filed June 18, 1998 ("the priority application").

I prepared the English translation of the above-identified priority application and I certify that the translation is a true and exact translation to the best of my knowledge and belief.

Date: May 9, 2006



JAKOB KUHN

Title: Patent Manager, ILFORD Imaging CH GmbH



Recording Sheets for Ink Jet Printing

Field of the Invention

- This invention relates to recording sheets for the ink jet printing process and to
- 5 coating compositions for the preparation of ink-receiving layers for this process. In particular, it relates to recording sheets where the image recorded thereon can be observed by both reflected or transmitted light, and where the recording sheets consist of a support onto which is coated at least one ink-receiving layer, and at
- 10 least one of these layers contains a porous inorganic oxide and an aliphatic hydroxycarboxylic acid with more than 2 carbon atoms.

Background of the Invention

- Recording sheets for the ink jet printing process available today do not have all
- 15 the required properties. In particular, there is an urgent need to improve the ink absorption capacity, ink absorption rate, image quality, water fastness and light stability. A preferred embodiment of the invention relates to improved recording sheets having excellent image quality, high ink absorption capacity and high ink absorption rate. In particular, recording sheets for ink jet printing are sought where
- 20 the images recorded thereon are resistant to rubbing on the surface and where the image is not altered or destroyed even when it is in contact with water or light.

Ink jet printing processes are of two different types: continuous stream and drop-on-demand.

- In continuous ink jet printing, ink is emitted in a continuous stream under pressure
- 25 through a nozzle. The stream breaks up into individual droplets at a fixed distance from the nozzle. The droplets are charged in accordance with digital data signals and passed through an electric field, which adjusts the trajectory of each droplet in order to direct it to a gutter for recirculation or to a specific location on the recording sheet.

- 30 In non-continuous ink jet printing, or the so-called "drop-on-demand" process, a droplet is expelled from a nozzle to a desired position on the recording sheet in accordance with digital data signals. A droplet is not formed or expelled unless it is to be deposited on the recording sheet.

- The invention relates to recording sheets and coating compositions that may be
- 35 used in both recording processes.

Recording sheets for ink jet printing must fulfill a number of stringent demands. The printed image needs to have the following properties:

- High resolution
- High color density
- Good color reproduction
- High resistance to rubbing
- 5 - Good water fastness
- High light stability

The following conditions have to be met to attain these objectives:

- 10 1. The ink needs to be absorbed quickly into the recording sheet.
2. The jetted ink droplets have to spread circularly on the recording sheet and have to form well-defined edges.
3. Dye diffusion in the recording sheet has to be low so that the diameter of the color points is not increased more than necessary.
- 15 4. An ink droplet is not allowed to interfere with a droplet deposited earlier nor should it blur it.
5. The recording sheet needs to have a surface that gives high color density and brilliance.
6. The recording sheet has to show excellent physical properties before and after printing.
- 20 7. The printed recording sheet is not allowed to change under the influence of light.

Recording sheets, which contain in at least one layer a porous inorganic oxide, 25 show a particularly high ink absorption rate and good dye fixing. Pseudo-bohemite, an agglomerate of aluminum oxide/hydroxide of formula $\text{Al}_2\text{O}_3 \cdot n \text{H}_2\text{O}$ ($n = 1$ to 1.5) is particularly preferred as the inorganic porous oxide. Recording sheets of this kind are described for example in patent applications EP 0'298'424, EP 0'407'720 and EP 0'500'021. However, these recording sheets show a great dis- 30 advantage in that the dyes used in the ink jet printing process have a bad light stability.

In order to prevent yellowing of recording sheets containing such porous oxides, patent application EP 0'614'771 proposes the addition of organic acids having a first dissociation coefficient of at most 5 wherein these acids contain an aromatic 35 ring or at least two carboxyl groups. Particularly preferred are acids with a first dissociation coefficient situated between 2 and 5.

Patent US 4'775'594 describes the addition of non-volatile organic acids to transparent recording sheets for ink jet printing to improve the wettability of such a recording sheet by the inks.

5 Patent application EP 0'410'051 describes a paper, where the printability (adhesion of printing dyes) is improved by the presence of a surface layer containing cinnamic acid or cinnamic acid derivatives.

Patent application EP 0'585'345 proposes the addition of dithiocarbamates, thiurams, thiocyanates or sterically hindered amines to recording sheets containing porous inorganic oxides in order to improve light stability.

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All these proposed methods, however, only give a marginal improvement of light stability of images printed by an ink jet printing process onto recording sheets containing porous inorganic oxides.

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Summary of the Invention

An objective of the present invention is to provide recording sheets for ink jet printing which have a high ink absorption capacity, a high ink absorption rate, an excellent image quality, an excellent water fastness and an excellent light stability.

20 A further objective is to provide recording sheets showing an excellent image quality with all the ink jet printers available on the market today.

The invention solves this task by providing a recording sheet for ink jet printing, having coated onto a support one or more layers containing a porous inorganic oxide and an aliphatic hydroxycarboxylic acid with more than 2 carbon atoms. The porous inorganic acid and the aliphatic hydroxycarboxylic acid may be present in the same layer or in different layers.

25 Colloidal silicon dioxide, colloidal aluminum oxide or colloidal aluminum oxide/hydroxide may be used as porous inorganic oxide. Colloidal aluminum oxide or colloidal aluminum oxide/hydroxide are preferred. Particularly preferred as colloidal aluminum oxide is γ -Al₂O₃ or a colloidal aluminum oxide/hydroxide modified with salts of the rare earth metal series as described in European patent application 98810383.4. A particularly preferred aluminum oxide/hydroxide is pseudo-bohemite, an agglomerate of aluminum oxide/hydroxide of formula Al₂O₃ • n H₂O, where n is from 1 to 1.5, or pseudo-bohemite modified with the salts of the rare earth metal series as also described in European patent application 35 98810383.4.

The aliphatic hydroxycarboxylic acid with more than 2 carbon atoms may be incorporated in different ways into the recording sheets.

One possibility is the direct addition to the coating solutions that are subsequently coated onto the support.

It is also possible to react the porous inorganic oxide in a separate step in aqueous solution with the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms before it is added to the coating solution, for example by heating under reflux.

Particularly preferred is the method where an aluminum alkoxide is hydrolyzed to pseudo-bohemite in the presence of the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms in a similar process as described in patent US 5'354'634.

Preferred aliphatic hydroxycarboxylic acids are water-soluble monohydroxymonocarboxylic acids.

2-Hydroxypropionic acid is particularly preferred as water-soluble monohydroxymonocarboxylic acid.

The invention is explained in detail in the following detailed description.

Detailed Description of the Invention

The invention describes a recording sheet for ink jet printing, having coated onto a support one or more layers containing a porous inorganic oxide and, in addition, an aliphatic hydroxycarboxylic acid with more than 2 carbon atoms. The porous inorganic oxide and the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms may be present in the same layer or in different layers.

Colloidal silicon dioxide, colloidal aluminum oxide or colloidal aluminum oxide/hydroxide may be used as porous inorganic oxide. Colloidal aluminum oxide or colloidal aluminum oxide/hydroxide are preferred. Especially preferred as colloidal aluminum oxide is $\gamma\text{-Al}_2\text{O}_3$ and as colloidal AlOOH an AlOOH modified with salts of the rare earth metal series as described in European patent application 98810383.4. This porous aluminum oxide/hydroxide contains one or more elements of the rare earth metal series of the periodic system of the elements with atomic numbers 57 to 71, preferably in an amount from 0.4 to 2.5 mole percent relative to Al_2O_3 . Particularly preferred as aluminum oxide/hydroxide is pseudo-bohemite, an agglomerate of aluminum oxide/hydroxide of formula $\text{Al}_2\text{O}_3 \cdot n \text{H}_2\text{O}$ where n is from 1 to 1.5, or pseudo-bohemite modified with the salts of the rare earth metal series as also described in European patent application 98810383.4. This porous pseudo-bohemite contains one or more elements of the rare earth metal series of the periodic system of the elements with atomic numbers 57 to 71, preferably in an amount from 0.4 to 2.5 mole percent relative to Al_2O_3 .

The aliphatic hydroxycarboxylic acid with more than 2 carbon atoms may be incorporated by different methods into the recording sheets.

One possibility is the direct addition to the coating solutions that are subsequently coated onto the support. Here, the value of pH of the coating solutions is adjusted by the addition of the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms to a value between 2.5 and 5.5, preferably to a value between 3.0 and 5.0.

- 5 It is also possible to react the porous inorganic oxide in a separate step in aqueous solution by heating under reflux with the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms, before it is added to the coating solution. Here, the value of pH of the aqueous solution is adjusted by the addition of the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms to a value between 2.5 and
10 4.0, preferably to a value between 2.5 and 3.5.

Particularly preferred is the method wherein an aluminum alkoxide is hydrolyzed in the presence of the organic hydroxycarboxylic acid with more than 2 carbon atoms in a similar process as described in patent US 5'354'634. This hydrolysis is carried out preferentially in a range of pH from 2.5 to 6.0; especially preferred is the range
15 of pH from 3.0 to 5.0. The value of pH is adjusted to the desired value by addition of the aliphatic hydroxycarboxylic acid.

Preferred aliphatic hydroxycarboxylic acids with more than 2 carbon atoms are water-soluble monohydroxymonocarboxylic acids.

- 2-Hydroxypropionic acid is particularly preferred as water-soluble monohydroxymonocarboxylic acid with more than 2 carbon atoms.
20

The recording sheets according to the invention contain in the coated layers, in addition to the porous inorganic oxide and the water-soluble aliphatic hydroxycarboxylic acid, one or more binders.

- 25 These binders normally are water-soluble polymers. Particularly preferred are film-forming polymers.

These water-soluble polymers include for example natural polymers or modified products thereof such as albumin, gelatin, casein, starch, gum arabicum, sodium or potassium alginate, hydroxyethylcellulose, carboxymethylcellulose, α -, β - or γ -cyclodextrine and the like. In the case where one of the water-soluble polymers is gelatin, all known types of gelatin may be used as for example acid pigskin gelatin or limed bone gelatin, acid or base hydrolyzed gelatin, but also derivatised gelatins such as phthalaoylated, acetylated or carbamoylated gelatin or gelatin derivatised with the anhydride of trimellitic acid.
30

- 35 A preferred natural binder is gelatin.

Synthetic polymers may also be used and include for example polyvinyl alcohol; polyvinyl pyrrolidone, completely or partially saponified products of copolymers of vinyl acetate with other monomers; homopolymers or copolymers of unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, crotonic acid and the like;

homopolymers or copolymers of vinyl monomers of sulfonated vinyl monomers such as vinylsulfonic acid, styrene sulfonic acid and the like. Furthermore, homopolymers or copolymers of vinyl monomers of (meth)acrylamide; homopolymers or copolymers of other monomers with ethylene oxide; polyurethanes; polyacrylamides; water-soluble nylon type polymers; polyesters; polyvinyl lactams; acrylamide polymers; substituted polyvinyl alcohol; polyvinyl acetals; polymers of alkyl and sulfoalkyl acrylates and methacrylates; hydrolyzed polyvinyl acetates; polyamides; polyvinyl pyridines; polyacrylic acid; copolymers with maleic anhydride; polyalkylene oxides; methacrylamide copolymers and maleic acid copolymers may be used. All these polymers may also be used as mixtures.

Preferred synthetic binders are polyvinyl alcohol and polyvinyl pyrrolidone or their mixtures.

These polymers may be blended with water insoluble natural or synthetic high molecular compounds, particularly with acrylate latices or with styrene acrylate latices.

Although not specifically claimed in this invention, water insoluble polymers are nevertheless considered part of the system.

The polymers mentioned above having groups with the possibility to react with a cross-linking agent may be cross-linked or hardened to form essentially water insoluble layers. Such cross-linking bonds may be either covalent or ionic. Cross-linking or hardening of the layers allows for the modification of the physical properties of the layers, like for instance in water absorption of the layer or in resistance against physical damage.

The cross-linking agents or hardeners are selected depending on the type of water-soluble polymers used.

Organic cross-linking agents and hardeners include for example aldehydes (such as formaldehyde, glyoxal or glutaraldehyde), N-methylol compounds (such as dimethylol urea or methylol dimethylhydantoin), dioxane derivatives (such as 2,3-dihydroxy dioxane), reactive vinyl compounds (such as 1,3,5-trisacryloyl hexahydro-s-triazine or bis-(vinylsulfonyl) methyl ether), active halogen compounds (such as 2,4-dichloro-6-hydroxy-s-triazine), epoxydes, aziridines, carbamoyl pyridinium compounds or mixtures of two or more of the above mentioned cross-linking agents.

Inorganic cross-linking agents or hardeners include for example chromium alum, aluminum alum or boric acid.

The layers may also contain reactive compounds that cross-link the layers under the influence of UV light, electron beams, X-ray beams or heat.

The layers may further be modified by the addition of fillers. Possible fillers used are for instance kaolin, talcum, Ca- or Ba-carbonates, silicon dioxide, titanium di-

oxide, bentonites, zeolites, aluminum silicate, calcium silicate or colloidal silicon dioxide. It is also possible to use organic inert particles such as polymer beads. These beads may consist of polyacrylates, polyacrylamides, polystyrene or different copolymers of acrylates and styrene. The fillers are selected according to the
5 intended use of the printed images. Some of these compounds cannot be used if the printed images are to be used as transparencies. Alternatively, they are of interest in cases where the printed images are to be used as remission pictures. Very often, the use of such fillers causes a wanted matte surface.

The recording sheets may further contain water-soluble metal salts, as for example
10 salts of the alkaline earths or salts of the rare earth metal series.

The recording sheets according to the invention have a support onto which is coated at least one ink-receiving layer. A wide variety of supports is known and commonly used in the art. They include all those supports that are used in the manufacture of photographic materials. This includes clear films made from cellulose
15 esters such as cellulose triacetate, cellulose acetate, cellulose propionate or cellulose acetate/butyrate, polyesters such as polyethylene terephthalate, polyamides, polycarbonates, polyimides, polyolefins, polyvinyl acetals, polyethers, polyvinyl chloride and polysulfonamides. Polyester films and particularly polyethylene terephthalate are preferred because of their excellent dimensional stability characteristics. The usual supports used in the manufacture of opaque photographic material may be used, including for example baryta paper, polyethylene coated papers, voided polyester such as MELINEX® manufactured by ICI. Particularly preferred are polyolefin coated papers or voided polyester.

With these supports, in particular polyester, a subbing layer is advantageously
25 added first to improve the bonding of the ink-receiving layers to the support. Useful subbing compositions for this purpose are well known in the photographic art and include for example terpolymers of vinylidene chloride, acrylonitrile and acrylic acid or of vinylidene chloride, methyl acrylate and itaconic acid.

Plain papers, comprising all different types of papers varying widely in their composition and in their properties, may also be used as supports. Pigmented papers
30 and cast-coated papers may be used as well as metal foils, such as foils made from aluminum.

The ink-receiving layers according to the invention are coated in general from aqueous solutions or dispersions containing all necessary ingredients. In many
35 cases, surfactants are added to those coating solutions or dispersions allowing for smooth coating and evenness of the layers. Suitable surfactants are described in many patents, as, for example, US patents 2'240'472, 2'271'623, 2'288'226, 2'739'891, 2'823'123, 2'831'766, 2'944'900, 3'068'101, 3'133'816, 3'158'484, 3'210'191, 3'253'919, 3'294'540, 3'415'649, 3'441'413, 3'475'174, 3'507'660, 40 3'545'974, 3'589'906, 3'666'478, 3'671'247, 3'726'683, 3'754'924, 3'756'828,

3'772'021 and 3'843'368; GB patents 1'012'495, 1'022'878, 1'138'514, 1'159'825, 1'179'290, 1'198'450, 1'374'780 and 1'397'218, and BE patent 731'126.

Besides being necessary for coating purposes, these compounds may have an influence on the image quality and may therefore be selected with this specific ob-
5 jective in mind. Although not specifically claimed in this invention, surfactants nevertheless form an important part of the invention.

In addition to the above mentioned ingredients, recording sheets according to the invention may contain additional additives aimed at further improving its performance, as for example brightening agents to improve the whiteness, such as stil-
10 benes, coumarines, triazines, oxazoles or others compounds known to someone skilled in the art.

Light stability may be improved by the addition of UV absorbers such as benzotri- azoles, benzophenones, thiazolidones, oxazoles, thiazoles and other compounds known to someone skilled in the art. The amount of UV absorber may vary from
15 200 to 2000 mg/m², preferably from 400 to 1000 mg/m². The UV absorbers may be added to any of the layers of the recording sheet according to the invention. It is preferred, however, if they are added, that the UV absorbers are included in the topmost layer of the system.

It is further known that images produced by ink jet printing may be protected from degradation by the addition of light stabilizers and antioxidants. Examples of such
20 compounds are sterically hindered phenols, sterically hindered amines, chromanols and the like. The above-mentioned additives may be added as aqueous solutions to the coating solutions. In the case where these compounds are not water-soluble, they can be incorporated into the coating solutions by other common
25 techniques known in the art. The compounds may, for example, be dissolved in a water-miscible solvent such as lower alcohols, glycols, ketones, esters or amides. Alternatively, the compounds may be added to the coating solutions as fine dispersions, as oil emulsions, as cyclodextrine inclusion complexes or incorporated into latex particles.

30 Typically, the layers according to the invention have a thickness in the range of 0.5 to 100 μm dry thickness, in particular in the range of 5 to 50 μm .

The coating solutions may be coated onto the support by any number of suitable procedures. The coating methods include extrusion coating, air knife coating, doctor blade coating, cascade coating and curtain coating. The coating solutions may
35 also be applied using spray techniques. The ink-receiving layers can be built up from several single layers that may be coated one after the other or simultaneously. It is likewise possible to coat a support on both sides with ink-receiving layers. It is also possible to coat an antistatic layer or an anticurl layer on the back-side. The selected coating method is, however, not to be considered limiting for
40 the present invention.

Inks for ink jet printing consist in essence of a liquid vehicle and a dye or pigment dissolved or suspended therein. The liquid vehicle for inks employed for ink jet printing consists in general of water or a mixture of water and a water-miscible organic solvent such as ethylene glycol, higher molecular weight glycols, glycerol, dipropylene glycol, polyethylene glycol, amides, polyvinyl pyrrolidone, N-methylpyrrolidone, cyclohexyl pyrrolidone, carboxylic acids and their esters, ethers, alcohols, organic sulfoxides, sulfolane, dimethylformamide, dimethylsulfoxide, cello-solve, polyurethanes, acrylates and the like.

The non-water parts of the ink generally serve as humefactants, cosolvents, viscosity regulating agents, ink penetration additives or drying agents. The organic components have in most cases a boiling point, which is higher than that of water. In addition, aqueous inks used for printers of the continuous flow type may contain inorganic or organic salts to increase their electric conductivity. Examples of such salts include nitrates, chlorides, phosphates and salts of water-soluble organic acids such as acetates, oxalates and citrates. The dyes or pigments suitable for the preparation of inks useable with the recording sheets according to the invention cover practically all classes of known coloring compounds. Dyes or pigments typically used for this purpose are described in patent application EP 0'559'324. The recording sheets according to the invention are meant to be used in conjunction with most of the inks representing the state of the art.

Other additives present in inks are for instance surfactants, optical brighteners, UV absorbers, light stabilizers, biocides and polymeric compounds.

This description of the inks is for illustration only and is not to be considered as limiting for the purpose of the invention.

Coatings of the recording sheets according to the invention were prepared in the following way:

100 g/m² of each of the coating solutions (their preparation is described later on) were coated at a temperature of 40° C onto a transparent polyester support. The coated support was then dried for 60 minutes at a temperature of 30° C. All coatings contain 10 g/m² of colloidal aluminum oxide or colloidal aluminum oxide/hydroxide (calculated as Al₂O₃).

The following test procedure was used to evaluate the light stability of the recording sheets described herein.

Color patches of the 4 colors cyan, magenta, yellow and black were printed onto the transparent recording sheets according to the invention, as described later on in the examples, with the aid of an ink jet printer EPSON STYLUS™ COLOR 500 in transparent mode using original inks.

The printed samples were irradiated in an ATLAS Ci35A Weather-O-Meter® with a 6500 W Xenon lamp until a total illumination of 40 kJoule/cm² was reached. The density loss was measured with an X-Rite® densitometer. It is expressed as per cent loss of initial density. In one color black, density losses are given for the three color channels yellow, magenta and cyan in this order.

Examples

Example 1

10 a) Hydrolysis of aluminum isopropoxide

A mixture of 360 g of deionised water and 338 g of isopropanol was prepared in a glass vessel. 153g of aluminum isopropoxide (available from Fluka Chemie AG, Buchs, Switzerland) were added to this mixture at a temperature of 75° C and the resulting mixture was stirred for 4 hours at a temperature between 75° C and 15 78° C. Afterwards, the temperature was increased to 95° C and 1.5 g of 2-hydroxypropionic acid were added. The temperature was then reduced to between 75° C and 78° C and the mixture was kept under stirring at this temperature for 48 hours. Finally, the resulting colloidal solution was evaporated under vacuum. 43 g of a white solid with a content of 75.2 % of Al₂O₃ were obtained. The X-ray dif- 20 fraction spectrum was equivalent to the one of pseudo-bohemite of formula AlOOH.

b) Preparation of the coating solution

13.3 g of the dried solid of example 1a) were added under stirring at a temperature of 40° C to a mixture of 50 g of deionised water and 7.0 g of acetic acid 25 (17.65 %). Afterwards, 16 g of a solution of polyvinyl alcohol (7.5 % by weight, hydrolysis degree 98 - 99 %, molecular weight 85'000 to 146'000) (36,315-4, available from ALDRICH Chemie, Buchs, Switzerland) were added. The resulting solution was exposed to ultrasound for 3 minutes. The value of pH was adjusted to 3.3 with acetic acid and the total weight was adjusted to 100 g with deionised water.

30

Comparative Example A

a) Hydrolysis of aluminum isopropoxide

1 g of nitric acid (30 %) was used for the hydrolysis in place of the 1.5 g of 2-hydroxypropionic acid of example 1. 44.6 g of a white solid with a content of 35 77.2 % of Al₂O₃ was obtained. The X-ray diffraction spectrum was equivalent to the one of pseudo-bohemite of formula AlOOH.

b) Preparation of the coating solution

In place of the 13.3 g of the dried solid and of the 7.0 g of acetic acid (17.65 %) of example 1a) 12.953 g of the dried solid of example Aa) and 6.8 g of acetic acid (17.65 %) were used. The value of pH of the solution was 3.3.

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Comparative Examples B - K

a) Hydrolysis of aluminum isopropoxide

The hydrolysis was done as in comparative example A.

b) Preparation of the coating solutions

- 10 In place of the acetic acid (17.65 %) of comparative example A the acids listed in Table 1 were used. The value of pH was adjusted to 3.3 with the corresponding acid.

Comparative example no.	Acid
B	Propionic acid
C	Malonic acid
D	Succinic acid
E	Adipic acid
F	Maleic acid
G	Oxalic acid
H	L(+)-Tartric acid
I	Phthalic acid
J	Glycolic acid
K	Hydroxymalonic acid

15

Table 1

Example 2

a) Hydrolysis of aluminum isopropoxide

The hydrolysis was done as in comparative example A.

- 20 b) Preparation of the coating solution

In place of the 6.8 g of acetic acid (17.65 %) of example Ab) 2.9 g of 2-hydroxy-propionic acid were used. The value of pH of the solution was 3.3.

Example 3

a) Hydrolysis of aluminum isopropoxide

The hydrolysis was done as in comparative example A.

b) Preparation of the coating solution

- 5 After addition of the 2-hydroxypropionic acid as in example 2, the resulting solution was heated under reflux for 20 hours before the addition of the polyvinyl alcohol.

Example 4

10 Preparation of the coating solution

- 18 g of γ - Al_2O_3 (ALU C, available from DEGUSSA AG, Baar, Switzerland) (content 96.2 % Al_2O_3) were dispersed at room temperature under stirring in 63 g of deionised water. The value of pH was adjusted to 3.3 with 2-hydroxypropionic acid. Afterwards, the solution was heated under reflux for 20 hours. Then, 16 g of a solution of polyvinyl alcohol (7.5 % by weight, hydrolysis degree 98 - 99 %, molecular weight 85'000 to 146'000) (36,315-4, available from ALDRICH Chemie, Buchs, Switzerland) were added, the resulting solution was exposed to ultrasound for 2 minutes, the value of pH was adjusted again to 3.3 with 2-hydroxypropionic acid and total weight was adjusted to 100 g with deionised water.

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Comparative Example L

Preparation of the coating solution

In place of the 2-hydroxypropionic acid of example 4, acetic acid was used.

25 Example 5

Preparation of the coating solution

- 5 g of the white solid of example 1a) were dispersed under stirring at a temperature of 20° C in 80 g of deionised water. Afterwards, 0.212 g of LaNO_3 (available from Fluka Chemie AG, Buchs, Switzerland) was added at a temperature of 90° C and the solution was stirred for a further 2 hours. The solution was evaporated under vacuum. A white solid was obtained, containing 0.222 mole percent of lanthanum.
- 13.83 g of this powder were added under stirring at a temperature of 40° C to a mixture of 57 g of deionised water and 6.81 g of acetic acid (17.65 %). Afterwards, 16 g of a solution of polyvinyl alcohol (7.5 % by weight, hydrolysis degree 98 - 99 %, molecular weight 85'000 to 146'000) (36,315-4, available from ALDRICH Chemie, Buchs, Switzerland) were added, the resulting solution was exposed to

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ultrasound for 3 minutes, the value of pH was again adjusted to 3.3 with acetic acid and the total weight was adjusted to 100 g with deionised water.

Comparative Example M

5 Preparation of the coating solution

In place of 5 g of the white powder of example 1a), 5.1 g of the white powder of comparative example A were used.

10 The results of the light stability tests are listed in Table 2 for the case where pseudo-bohemite was used as inorganic porous oxide.

Example No.	Density Loss in per cent					
	Yellow	Magenta	Cyan	Black		
1	18	23	16	31	35	45
2	15	30	10	33	42	50
3	21	33	11	31	39	49
A	20	42	20	44	58	68
B	20	44	20	44	54	64
C	26	40	20	41	49	60
D	30	46	19	50	61	69
E	24	40	25	51	60	71
F	25	38	23	50	59	68
G	25	36	25	54	64	71
H	24	34	21	28	57	67
I	24	35	21	53	61	70
J	23	35	23	47	59	66
K	28	37	36	53	63	69

Table 2

15 A comparison of the results of Table 2 shows that, in the case where pseudo-bohemite was used as porous inorganic oxide, the addition of 2-hydroxypropionic

acid according to the invention to the recording sheets (examples 1 - 3) significantly improves the light stability of all 4 colors compared to recording sheets containing acids that are state of the art (examples A - K). This improvement occurs independently of the method how the 2-hydroxypropionic acid is added to the recording sheet.

The results of the light stability tests are listed in Table 3 for the case where γ - Al_2O_3 was used as inorganic porous oxide.

Example No.	Density Loss in per cent					
	Yellow	Magenta	Cyan	Black		
4	22	27	5	29	31	39
L	47	71	8	26	32	36

Table 3

A comparison of the results of Table 3 shows that, in the case where γ - Al_2O_3 was used as porous inorganic oxide, the addition of 2-hydroxypropionic acid according to the invention to the recording sheets (example 4) significantly improves the light stability of the 3 colors yellow, magenta and cyan compared to a recording sheet containing an acid that is state of the art (example L).

The results of light stability tests are listed in Table 4 for the case where pseudo-bohemite modified with lanthanum nitrate according to European patent application 98810383.4 was used as the inorganic porous oxide.

Example no.	Density Loss in %					
	Yellow	Magenta	Cyan	Black		
5	22	39	7	17	14	21
M	27	81	31	25	16	29

Table 4

A comparison of the results of Table 4 shows that, in the case where pseudo-bohemite modified with lanthanum nitrate was used as porous inorganic oxide, the

addition of 2-hydroxypropionic acid according to the invention to the recording sheets (example 4) significantly improves the light stability of all 4 colors in comparison to a recording sheet containing an acid that is state of the art (example M).

- 5 Other trials, where the value of pH of the coating solution was varied, gave very similar same results as in the examples and comparative examples mentioned above.

CLAIMS

1. Recording sheet for ink jet printing, having coated onto a support at least one ink-receiving layer containing a porous inorganic oxide and an aliphatic hydroxycarboxylic acid with more than 2 carbon atoms.
5
2. Recording sheet according to claim 1, characterized in that the aliphatic hydroxycarboxylic acid with more than 2 carbon atoms is a water-soluble monohydroxymonocarboxylic acid.
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3. Recording sheet according to claim 2, characterized in that the water-soluble monohydroxymonocarboxylic acid is 2-hydroxypropionic acid.
4. Recording sheet according to claims 1 to 3, characterized in that the porous inorganic oxide is colloidal aluminum oxide or colloidal aluminum oxide/hydroxide.
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5. Recording sheet according to claims 1 to 3, characterized in that the porous inorganic oxide is colloidal γ -Al₂O₃.
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6. Recording sheet according to claims 1 to 3, characterized in that the porous inorganic oxide is pseudo-bohemite.
7. Recording sheet according to claims 1 to 3, characterized in that the porous inorganic oxide is AlOOH or pseudo-bohemite containing at least one element of the rare earth metal series of the periodic system of the elements with atomic numbers 57 to 71, preferably in an amount of from 0.04 to 4.2 mole percent relative to Al₂O₃.
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8. Recording sheet according to claims 6 and 7, characterized in that the pseudo-bohemite is prepared by hydrolysis of aluminum isopropoxide in the presence of the hydroxycarboxylic acid.
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9. Recording sheet according to claims 1 to 8, characterized in that the binders are gelatin, polyvinyl alcohol or polyvinyl pyrrolidone or mixtures thereof.
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10. Coating compositions for the preparation of an ink-receiving layer for a recording sheet for ink jet printing according to claims 1 to 9.

Abstract

A recording sheet for ink jet printing is described consisting of a support onto which is coated at least one ink-receiving layer, wherein at least one ink-receiving layer contains a porous inorganic oxide, characterized in that the recording sheet contains an aliphatic hydroxycarboxylic acid with at least 2 carbon atoms.